SEPARATION OF FERMENTATION PRODUCTS USING BATCH DISTILLATION

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ABSTRACT

This research aims to study the separation processes of fermentation products by using batch distillation. Technically, the main objective of the research is to study behavior of the purification of fermentation products of local nira by utilizing batch distillation . The major product from the fermentation process is ethanol. The scope of study includes the investigation of composition profile of the distillate and the others parameter to the composition profile. Nira is a fermentation product that to be expected to produce ethanol by undergo the separation process using batch distillation. The result shows the concentration can be obtained by using the standard curve . By utilizing batch distillation, the optimun condition in separation components in vinegar from nypa palm can be determine. For the effect of time the concentration of ethanol become concentrated as increasing the time. At 74˚C-76˚C the optimum product can be collected because in this stage the particle of ethanol have been nearly reached the boiling point which means the particle have enough energy to escape from the liquid form to the vapors form. The concentration of acetic acid is higher than ethanol because most of ethanol particle have been converted to the acetic acid. The highest ethanol concentration should be after 20 hours fermentation, however the vinegar solution that has been used in this experiment is more than 1 days.

ABSTRAK

Kajian ini fokus untuk mengkaji process pemisahan produk penapaian menggunakan penyulingan berperingkat. Secara teknikal, objektif untuk kajian ini adalah untuk mengkaji sifat penulenen produk penapaian dari produk tempatan iaitu cuka nipah menggunakan penyulingan beperingkat. Produk utama untuk proses penapaian ini ialah etanol. Skop kajian merangkumi kajian kandungan produk dari penyulingan dan parameter untuk menghasilkan produk. Cuka nipah dijangka menghasilkan etanol menggunakan penyulingan beperingkat. Hasilnya kepekatan boleh didapati melalui lengkung standard . dengan menggunakan penyulingan beperingkat keadaan optimum dalam process pemisahan komponen didalam cuka nipah boleh di dapati. Untuk kesan perubahan masa , kepekatan etanol bertambah apabila masa bertambah. Pada suhu 74℃-76℃ kepekatan produk adalah paling tinggi kerana partikel etanol menghampiri takat didih dan bermakna partikel mempunyai cukup tenaga untuk terbebas dari keaadaan cecair kepada gas. Kepekatan asid asetic lagi tinggi daripada etanol kerana partikel etanol telah bertukar kepada asid asetic. Kepekatan etanol paling tinggi sepatutnya selepas 20 jam proses penapaian, tetapi larutan cuka yang digunakan dalam eksperimen ini melebihi satu hari.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1: Introduction

The reasearch objective is to determine the behavior of the purification of fermentation products of local nira by utilizing batch distillation process. Fermentation can produce alcohol (ethanol) by undergoing continuosly fermenting unit. Ethanol is commonly prepared by fermentation of sugars or other biomass feedstock. In fermentation process fermentable materials are added with microbe. During the fermentation, the microbe cells consume the biomass feedstock in beaker and convert the feedstock into the alcohol as they continue to grow.

Fermentation processes from any material that contains sugar could derive ethanol. The varied raw materials used in the manufacture of ethanol via fermentation are conveniently classified into three main types of raw materials: sugars, starches, and cellulose materials. Sugars (from sugarcane, sugar beets, molasses, and fruits) can be converted into ethanol directly by Yan Lin & Shuzo Tanaka et al, 2005.

Starches that from corn, cassava, potatoes, and root crops must first be hydrolyzed to fermentable sugars by the action of enzymes from malt or molds. Cellulose (from wood, agricultural residues, waste sulfite liquor from pulp, and paper mills) must likewise be converted into sugars, generally by the action of mineral acids. Once simple sugars are formed, enzymes from microorganisms can readily ferment them to ethanol (Yan Lin & Shuzo Tanaka et al, 2005).

Fermentation product:

$$C_6H_{12}O_6 \longrightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

It is usually carried out in a batch still to which a column equivalent to a number of equilibrium stages is attached. In a batch distillation process, operation occur discontinuously. In contrast with a continuous process, a batch process does not deliver its product continuously but in discrete manner. This means that mass, temperature, concentration, and other properties vary with time. Batch process is economical if it is in small volume. Batch process are made up from a series of batch and semicontinues steps. So, the process is flexible in changing production rate or product formulation. For any process synthesis the prediction of the concentration path of distillate and bottom of a batch distillation is necessary especially for mixtures with complex structure, e.g. with one ore more azeotropes. Many authors have investigated these concentration paths (Reinders and de Minjer, 1940; Ewe11 and Welch, 1945). Some of their results can be explained by a modified Rayleigh equation (herepresented for batch distillation operated as stripping column):

$$\frac{dx_{Da}}{dx_{Db}} = \frac{x_{Da} - x_{Ba}}{x_{Db} - x_{Bb}}$$

The demand of the ethanol production and consumption has grown considerably mainly as a renewable fuel. As ethanol is soluble in water, it can be used in a variety of different products in industry. By using batch distillation process behavior the optimal condition could be determined to obtain ethanol.

1.2: Problem Statement

The ethanol produced by fermentation ranges in concentration from a few percent up to about 14 percent by Shakhashiri et al.,2009. Nearly all fuel ethanol is produced by fermentation of corn glucose in the US or sucrose in Brazil by MacDonald et al, 2001 and Rosillo-Calle & Cortez et al, 1998. A latest technology is used for a country with a significant agronomic-based economy for fuel ethanol fermentation. This is possible because, during the last two decades, technology for ethanol production has been developed to the point at which large-scale production will be a reality in the next few years.

In order to improve the production of ethanol by separation the fermentation product, batch distillation is suitable in less production. Batch distillation can be adjusted the temperature and the feed of raw material.

1.3: Objective

The main objective of the research is to study behavior of the purification of fermentation products of local ‘nira’ by utilizing batch distillation . By utilizing batch distillation, the optimun condition in separation components in ‘nira’.

1.4: Scope of Study

This research will be carry out by divided into four step. Firstly is preparation of raw material, secondly is check the standard solution concentration of ethanol and acetic acid by using UV-Vis spectrophotometers , followed by study the effect of parameters in distillation process and lastly check the product concentration again by using UV-Vis spectrophotometers.

Preparation of raw material is done by filter the vinegar from nypa palm by using vacuum filter. This process will avoid any impurities in the solution. Secondly is to check the standard solution for the ethanol by plotting the graph at different concentration versus absorbent. Thirdly is study the composition profile of distillate as a function of time. Lastly, the concentration for ethanol and acetic acid will be collected by compare absorbent from UV-Vis spectrophotometers to the standard graph solution.

1.5: Rationale and Significance

The world's ethanol production is continually drop in 2012 and will continue to next 2 years. This basically means that to make up for that loss some analysts think a new demand source is needed if the prices continue to remain in the current price range. Ethanol demand keep increasing due to the used extensively as a solvent in the manufacture of varnishes and perfumes, as a disinfectant and mostly used for gasoline additive and furthermore, ethanol is less toxic than the other alcohols. The depletion of world energy supply creates interest to find alternative source to produce ethanol.

By utilizing the optimum batch distillation, the production ethanol will be increase. The parameter was studied in order to find the better condition in production of ethanol. The separation could occur due to the differential of boiling point of water that is 100 ^{o}C at the atmospheric pressure. It has been recognized that if ethanol separation is combined with fermentation there will be a reduction in the cost of process. When ethanol is removed directly from the fermentor, or by recycling the contents of a continuous fermentor through a separation device, which retains cell viability, it is possible to completely convert a much more concentrated feed .

CHAPTER 2

LITERATURE REVIEW

2.1 Distillation

Distillation of a feed mixture in given composition is placed in a single stage separator (a still pot, retort or flask) and is heated to boiling. The vapor is collected and condensed to a distillate. The composition of the remaining liquid and the distillate product are determined by expressed in functions of time. There are several reasons for running a batch process such as this:

1) Small capacity doesn't warrant continuous operation

2) Separation is to be done only occasionally

3) Separation is preparative to produce a new product

4) Upstream operations are batch wise or feed stocks vary with time or from batch to batch

5) Feed materials are not appropriate for a continuous flow system.

Integrates both sides:

$$\int \frac{dx}{x(k-1)} = \int \frac{dW}{W} \longrightarrow \frac{1}{(k-1)} \ln \frac{x}{x_0} = \ln \frac{w}{w_0}$$

2.2 Alcohol

Alcohol are compounds in which one or more hydrogen atoms in alkane have been replaced by an –OH group.the point of an alcohol is always much higher than alkane with the same number of carbon atoms. The boiling points of the alcohols increase as the number carbon atoms increases (Jim Clark,2003).

Alcohol is a process of separation alcohol (more volatile) from water (less volatile) from the solution. The solution will be heated and condesated the alcohol at the distillate will be collected as a high alcohol strength liquid. The volatilities of the substances from the distillation process deviate predicted by using Raoult's Law. In batch distillation, the separation of two components will stop when the volatilities become same and the boiling point remains static.

2.3 Properties of Ethanol

Ethanol and water form a constant boiling point of the mixture at 95.6% v/v EtOH with a boiling point 78.2 ^{o}C . This temperature is close with the boiling point of pure ethanol that is 78.5^{o}C (Shakhashiri et al.,2009). The separation could occur due to the differential of boiling point of water that is 100 ^{o}C at the atmospheric pressure.

Ethanol is a monohydric primary alcohol. It melts at -117.3°C and boils at 78.5°C. It is miscible with water in all proportions and is separated from water only with difficulty; ethanol that is completely free of water is called absolute ethanol. Ethanol forms a constant-boiling mixture, or azeotrope, with water that contains 95% ethanol and 5% water and that boils at 78.15°C; since the boiling point of this binary azeotrope is below that of pure ethanol, absolute ethanol cannot be obtained by simple distillation. However, if benzene is added to 95% ethanol, a ternary azeotrope of benzene, ethanol, and water, with boiling point 64.9°C, can form; since the proportion of water to ethanol in this azeotrope is greater than that in 95% ethanol, the water can be removed from 95% ethanol by adding benzene and distilling off this azeotrope (Ang Dek Chang et al.,2001).Because small amounts of benzene may remain, absolute ethanol prepared by this process is poisonous.

Ethanol reacts with certain acid to form ester, with acetic acid it forms ethyl acetate. Ethanol can also be oxidise to form diethyl ether or at higher temperature , ethylene (The Columbia Electronic Encyclopedia, 2000).

2.4 Ethanol Fermentation

Ethanol is well known for use in alcoholic beverages, and the vast majority of ethanol for use as fuel, is produced by fermentation. By using yeast that usually *Saccharomyces cerevisiae*, the reaction occur to metabolize sugar in the absence of oxygen and then they produce ethanol and carbon dioxide. The chemical equation below summarizes the conversion:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3CH_2OH + 2\ CO_2$$

It has been recognized that if ethanol separation is combined with fermentation there will be a reduction in the cost of process. When ethanol is removed directly from the fermentor, or by recycling the contents of a continuous fermentor through a separation device, which retains cell viability, it is possible to completely convert a much more concentrated feed .

Ethanol could be produced either synthetically by direct hydration of ethylene which is a product of natural gas, or by fermentation process which involved the conversion of fermentable sugar into ethanol by microorganism such as Zymomonas mobilis and Saccharomyces cerevisiae. Except for human consumption, synthetic ethanol is widely used due to its lower production costs. However, the synthetic ethanol is relied on non-renewable resources. Therefore, if ethanol is to be widely used as a chemical feedstock and as fuel in future, the production of ethanol via fermentation process using renewable biomass is essential (Ang Dek Chang,2001).

2.5 Ethanol Uses In Chemical Industry

Ethanol has been used in about 50-60% in industrial field as a solvent in the formulation of numerous commercial products. Fermentation ethanol is preferred for use in the formulation of medicinal products such as tincture of iodine , merthiolate , cough syrups , and elixirs (Herman Harry Szamant,1989)

15 % of industrial uses ethanol is in production of esters. Carboxylic acids will be react with ethanol when warmed together in the presence of a few drops of concentrated sulphuric acid in order to observed the smell of the esters formed (Jim Clark, 2004).

Ethanol can be easily converted through dehydration process to produce diethyl ether (DEE) which is a source of compression-ignition fuel with higher energy density than from ethanol. In the trasportation sector , ethanol produced from the biomass as future fuel for spark-ignited engines because of high octane quality.

2.6 UV-Vis Spectrophotometer

Ultraviolet (UV) and Visible (VIS) light can cause electronic transitions. When a molecule absorbs UV-VIS radiation, the absorbed energy excites an electron into an empty, higher energy orbital. The absorbance of energy can be plotted against the wavelength to yield a UV-VIS spectrum. UV-VIS spectroscopy has many uses including detection of eluting components in high performance liquid chromatography (HPLC), determination of the oxidation state of a metal center of a cofactor , or determination of the maximum absorbance of a compound prior to a photochemical reaction. Most organic compounds that absorb UV-VIS radiation contain conjugated pi-bonds. Both the shape of the peak and the wavelength of maximum absorbance (l_{max}) give information about the structure of the compound (Department of Chemical Wake Forest College, 2012)

Ultraviolet radiation has wavelengths of 200-400 nm. Visible light has wavelengths of 400-800 nm. Plastic cuvettes can be used to hold a sample if you wish to scan only the visible region. Since plastic absorbs UV radiation, more expensive quartzcuvettes are used when ultraviolet scans are desired.

For conviniece of reference, definitions of various spectral regions have been set by Joint Comittee on Nomenclature in Applied Spectroscopy.

Table 2.1 :Wavelength For Various Spectral Regions

Region	Wavelength
Far ultraviolet	10-200
Near ultraviolet	200-380
Visible	380-780
Near infrared	780-3000
Middle infrared	3000-30,000
Far infrared	30,000-300,000
Microwave	300,000-1,000,000,000

Source: http://www.molecularinfo.com/MTM/UV.pdf

CHAPTER 3

METHODOLOGY

3.1 Chemical and Raw Material

Chemical used in this experiment are 1M acetic acid and 99.7% v/v pure ethanol. This chemical was used as the standard solution in order to find concentration of ethanol and acetic acid in nypa palm vinegar solution. The only material is a product fermentation that is vinegar from nypa palm. By utilizing the optimum batch distillation, the production of ethanol from the vinegar of nypa palm can be increase.

3.2 Equipment

In this study, there are some important equipment that is used. Firstly are vacuum pump suction, UV-Vis spectrophotometer and batch distillation. Vacuum pump suction is used to separate the impurities from the material to increase the accuracy. UV-Vis spectrophotometer is used to determine the concentration of ethanol and acetic acid in the solution of vinegar of nypa palm. Batch distillation is used to separate the components in the vinegar.

3.3 Experimental Procedure

3.3.1 Preparation of Raw Material

Initially , the solution of vinegar from nypa palm was removed the impurities by using vacuum pump suction. The solution will be filtered and the color of solution become clearrer. The impurities was removed because it may effect the result due to the disturbance that may occured.

3.3.2 Preparation Standard Curve

This process was including using the UV-Vis spectrophotometer to determine the concentration of solution. Acetic acid and ethanol solution was set at four different concentrations. The type of cuvette is glass because the wavelength for both acetic acid and ethanol is below than 350nm. By using UV-Vis spectrophotometer to determine the absorbent, the concentration versus absorbent was plotting. This graph then can be used to find the concentration of vinegar.

Figure 3.1: UV-Vis spectrophotometer

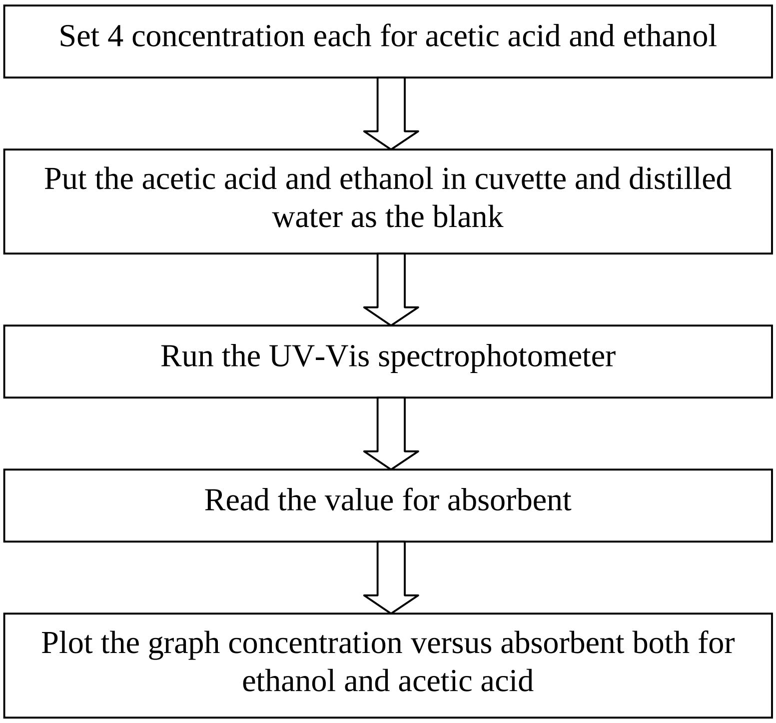

Figure 3.2: Preparation Standard Graph for Ethanol and Acetic Acid

3.3.3 Evaluation Parameter by Using Batch Distillation

This step is using batch distillation to separate components in vinegar. By conducting the batch distillation experiment, temperature and volume of vinegar was recorded each 30 minutes for four times. The product then was collected in order to find the concentration later by using UV-Vis spectrophotometer. The boiling point of ethanol is 78 ˚C so the experiment was stop when reaching the boiling point of ethanol.

Figure 3.3 : Batch Distillation Process

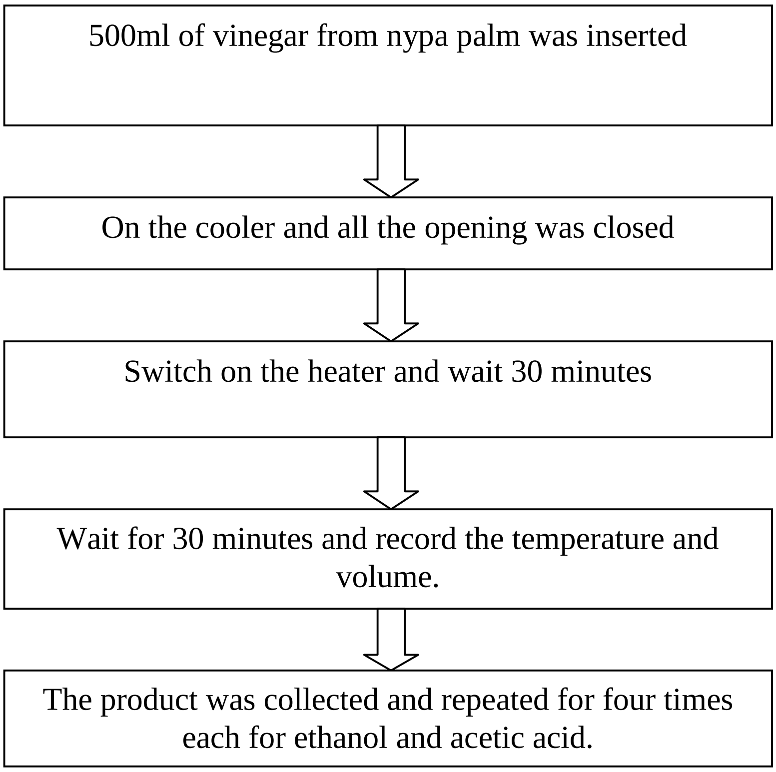

Figure 3.4 : Batch Distillation Process Step

3.3.4 Determine the Concentration

The concentration of ethanol and acetic acid will be determine by refering to the standard curve solution . Each 30 minutes, 60 minutes, 90 minutes and 120 minutes was collected the product sample. To determine the sample concentration once again UV-Vis spectrophotometer was used to find the concentration. The wavelength for ethanol is at 240 nm whereas acetic acid is 207 nm.

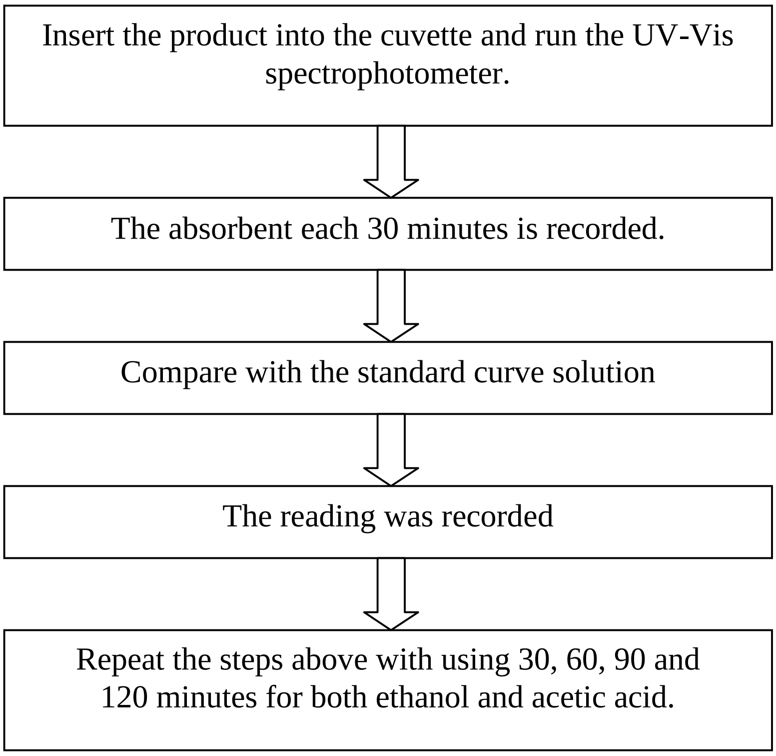

Figure 3.5: Determine the Concentration of Product

CHAPTER 4

RESULT AND DISCUSSION

4.1 Background

This chapter is discussed about the result obtained from the experiment. The experiment was repeated three times to compare the result. Each experiment will determine the concentration ethanol and acetic acid, temperature, and also volume collected for 30 minutes, 60 minutes, 90 minutes and 120 minutes. However the main result is to compare the concentration ethanol and acetic acid for each time.

4.2 Standard Curve

Standard curve is plotted for absorbent versus concentration in order to get the value of concentration for duration time parameters. Standard curve for ethanol is plotted using several of initial concentration starting from 19.94 g/L, 39.88 g/L, 59.82 g/L, and 79.76 g/L whereas the standard curve for acetic acid was 0.05 M, 0.10M,0.15 M and 0.2M. By using UV-Vis spectrophotometer, absorbent value can be obtained. This standard curve is used to predict the concentration at certain parameters for the others. **Table 4.1** shows the values for absorbent according to initial concentrations for ethanol while **Figure 4.1** in Appendix A shows the graph of absorbent versus concentration for ethanol. **Table 4.2** shows the values for absorbent according to initial concentrations for acetic acid starting from 0.05 M, 0.10 M, 0.15 M, and 0.2 M while **Figure 4.2** in appendix A shows the graph of absorbent versus concentration for acetic acid. The absorbent **Table 4.6** and **Table 4.7** for each experiment for ethanol and acetic acid in Appendix A.

Table 4.1: Absorbent for Standard Concentration Ethanol

Absorbent	Concentration (g/L)
0.786	19.94
1.082	39.88
1.401	59.82
1.724	79.76

Table 4.2: Absorbent for Standard Concentration Acetic Acid

Absorbent	Concentration (M)
0.196	0.05
0.347	0.10
0.525	0.15
0.717	0.20

4.3 Effect of Parameter

Appendix B shows the calculation of acetic acid concentration. By using the graph from **Figure 4.1** and **Figure 4.2** in Appendix A, the concentrations of acetic acid and ethanol in product can be determine at certain time. The result for the effect of parameter shows in **Table 4.3, Table 4.4,** and **Table 4.5**.

Table 4.3: Effect of Parameter in Batch Distillation Experiment 1

total volume = 500ml
temperature = 27 ˚C

Time, min	temp, ˚C	Conc. Ethanol, g/L	Conc. Acetic acid, g/L	volume ,ml
30	70	1.00	14.6522	49.2
60	72	1.60	14.7126	51.5
90	74	4.00	14.7723	56.2
120	78	5.00	14.8324	43.4

total= 200.3ml

residue= 235ml

Table 4.4: Effect of Parameter in Batch Distillation Experiment 2

Total volume = 500ml

Temperature = 27˚C

Time, min	temp, C	Conc. Ethanol, g/L	Conc. Acetic acid, g/L	volume ,ml
30	69	5.00	14.7126	50.00
60	73	5.40	14.7126	50.00
90	76	6.00	14.7126	57.40
120	78	6.30	14.7723	44.50

total= 200.9ml

residue=232ml